<Interface Science> Solutions and Interfaces

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- Solutions and Interfaces -

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Scope of Research

Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biological interests are systematically studied by NMR under extreme conditions. High pressures and high temperatures are employed to shed light on microscopic controlling factors for the structure and dynamics of solutions. Vibrational spectroscopic studies are carried out to elucidate structure and orientations of organic and water molecules in ultra-thin films. Static and dynamic NMR of endocrine disruptors, anesthetics, peptides, and proteins in lipid bilayer membranes, crystallization of protein monolayers, and advanced dispersion systems are also investigated.

Research Activities (Year 2002)

Presentations

Water and Solutions under Extreme Conditions

Supercritical Water Decarboxylation of Aliphatic and Aromatic Carboxylic Acids, Nakahara M, 2002 International Association for the Properties of Water and Steam, 23 July.

NMR Study on Aqueous Solutions of Electrolytes at High Temperatures and High Pressures, Wakai C, Nakao N, Kubo M, Matubayasi N, and Nakahara M, 2002 International Association for the Properties of Water and Steam, 23 July.

Raman Spectroscopic Study of Supercritical Hydrogen Bonding Fluids, Kubo M, Matubayasi N, and Nakahara M, 25th Symposium on Solution Chemistry of Japan, 26 September.

Structure, Dynamics, and Reactions of Supercritical Water, Matubayasi N, 25th Symposium on Solution Chemistry of Japan, 27 September.

Conformational Equilibria of Side Chains in Aspartic Acid Peptides and Achatin-I: Decomposition of the Thermodynamic Quantities, Sequence-Position Dependence, and Hydration Effect, Kimura T, Matubayasi N, and Nakahara M, 25th Symposium on Solution Chemistry of Japan, 27 September, and **26** related presentations in other meetings and symposia.

Ultra-thin Films

Effect of Infrared Radiation on FT-IR External Reflection Spectra of Langmuir Monolayers, Sakai H [Heian Jogakuin (Saint Agnes') College] and Umemura J, 55th Meeting of Colloid and Interface Chemistry, Japan, 14 September.

Dynamic NMR of Membrane-Drug Interactions

Solution NMR Studies on Distribution and Dynamics of Drugs in Membranes, Okamura E, 122th Annual Meet-

Topics

Raman spectroscopic studies of supercritical water and methanol:high-sensitivity observations over a wide density range

High-sensitivity Raman spectroscopic equipment is developed for the measurements of supercritical fluids. The system consists of a high-pressure chamber, a supercritical cell, a lens that collects back-scattered light, and a high-sensitivity Renishaw spectrometer connected to the collecting lens via fiber optic cable. The overview of the supercritical cell is shown in Fig.1. A specially manufactured thin diamond window enables an exceptionally wide solid angle observation so that the back-scattered light is collected by the detector with minimal loss. The new Raman cell system allows the vibrational analyses of supercritical water at 400°C and the density as low as 3.2×10^{-4} g/cm^3 (corresponding to the pressure of 0.1 MPa). With the novel equipment, the density dependence of OH stretching bands of supercritical water and methanol were investigated over a wide range of densities. The OH symmetric stretching band of supercritical water shows a nonlinear density dependence at ~0.2 g/cm^3 (corresponding to the reduced density of ~0.6) that was not observed in NMR chemical shift measurements. In contrast, the NMR chemical shift and the number of hydrogen bonds exhibit an excellent correlation with each other. The OH stretching band of supercritical methanol is generally related to the number of hydrogen bonds. From the fact that Raman spectroscopy and NMR chemical shift measurements show different density dependence, the number of hydrogen bonds cannot be a single representative indicator of the local structure.

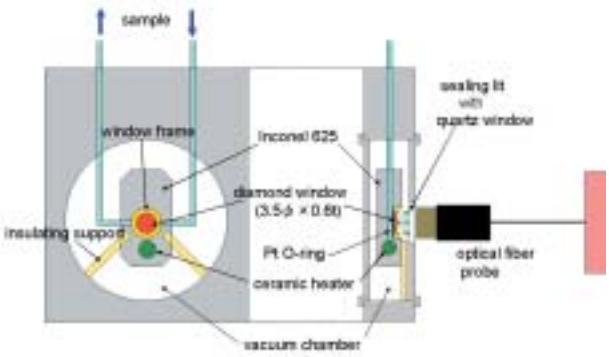

Fig. 1

Membrane dynamics and transport of endocrine disruptors and channel peptides

Membrane transport of endocrine disruptors (ED) and channel peptides is noninvasively detected by NMR. A high-resolution NMR combining pulsed-field-gradient technique shows how fast ED and peptides are transported in lipid bilayer vesicles, a good model for cell membrane. The transport of ED and channel peptides in membrane is not rapid but more than one order of magnitute as slow as that in solution. The transport is dominated by the membrane softness or fluctuation; the mobility is comparable to the membrane lipid diffusion. The success opens the possibility to monitor wide range of membrane transport phenomena; neither labeling nor probing is required.

ing of the Pharmaceutical Society of Japan, 26 March.

Static and Dynamic NMR Studies on Drugs and Endocrine Disruptors at Lipid Bilayer Interfaces, Nakahara M, NATO-ASI (EMLG/JMLG Annual Meeting): Novel Approaches to the Structure and Dynamics of Liquids, 12 September.

Dynamics of Lipid Bilayer Membranes and Drug Transport by NMR, Okamura E and Nakahara M, 55th Meeting of Colloid and Interface Chemistry, Japan, 14 September, and **2** related presentations in other symposia.

Grants

Nakahara M, Collaboratory on Electron Correlations - Toward a New Research Network between Physics and Chemistry, Grant-in-Aid for Creative Scientific Research, 1 April 2001 - 31 March 2006.

Nakahara M, Element Organic Reactions in Super- and Subcritical Water, Grant-in-Aid for Creative Scientific Research (B) (2), 1 April 2001 - 31 March 2003.

Hasegawa T and Umemura J, Study of Molecular Recognition Formed in Systematic Molecular Assemblies, The Japan-USA Joint Research Projects, 1 April 2000 - 31 March 2003.

Matubayasi N, Theory of Solutions in the Energy Representation from Ambient to Supercritical, Grant-in-Aid for Scientific Research (C) (2), 1 April 2001 - 31 March 2003.

Okamura E, Transport of Endocrine Disruptors in Phospholipid Bilayer Membranes, Grant-in-Aid for Scientific Research (C) (2), 1 April 2002 - 31 March 2004.

Wakai C, Inversion of Magnitude Relation of Translational and Rotaional Diffusion Coefficients for Organic Acids and Their Ions in Aqueous Solutions, Grant-in-Aid for Scientific Research for Young Scientists (B), 1 April 2002 - 31 March 2004.